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Transition probability for Ca ($4s\,6s\ ^1S \rightarrow 4s\,4p\ ^1P$)

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The emission, transition probability of the Ca ($4s\,6s\ ^1S \rightarrow 4s\,4p\ ^1P$) transition at 586.8 nm has been measured relative to the known strength of the Ca ($4p^2\ ^1D \rightarrow 4s\,4p\ ^1P$) transition at 585.7 nm by two-step laser excitation. The ratio of transition probabilities was found to be $A_{586.8}/A_{585.7} = (3.5 \pm 0.5) \times 10^{-1}$ resulting in an A value for the 586.8-nm transition of $2.35 \times 10^7\ \mathrm{sec}^{-1}$.

I. INTRODUCTION

Transition probabilities are important for spectral analysis and modeling in astrophysics and laser kinematics. In this paper a value is reported for the previously unmeasured emission, transition probability of Ca ($4s\,6s\ ^1S \rightarrow 4s\,4p\ ^1P$). Extensive transition probabilities for many Ca transitions have recently been published.[1,2] Extensive spectral data on the alkaline-earth elements have been generated by stepwise, multiphoton laser excitation and ionization techniques, but no transition probabilities or oscillator strengths were determined in these studies.[3] In this paper I report on the determination of an unknown transition probability by two-step laser excitation. First the method is presented, then the apparatus is described fully, and the results presented, analyzed, and compared with theory.

II. THEORY

The method employed in this experiment depends on populating the Ca $4s\,4p\ ^1P$ state with one laser and the selective excitation of either the $4s\,6s\ ^1S$ or $4p^2\ ^1D$ state by a second laser. The fluorescence back to the ^1P state is monitored for both transitions. Figure 1 shows a simplified Ca energy-level diagram with the transitions of interest. In this experiment the ^1P population is created by a N_2-pulsed dye laser tuned on resonance with the 422.7 nm transition in Ca. Excitation to the upper ^1S and ^1D states at 586.8 and 585.7 nm, respectively, is done by a cw, Ar^+-pumped dye laser. A single photomultiplier and interference filter are used to monitor fluorescence from these states at 586 nm. By tuning the cw laser between the two states the ratio of fluorescence intensities R_F can be determined. The relationship between the fluorescence ratio R_F and the transition probabilities or oscillator strengths can be easily derived.

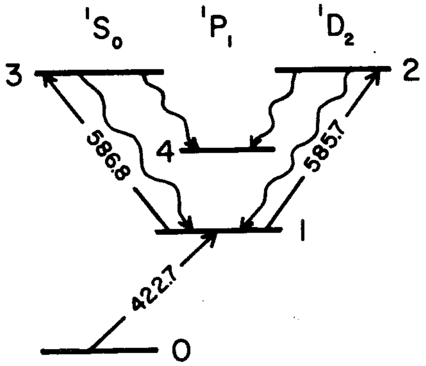

FIG. 1. Simplified energy-level diagram of the Ca singlet system. The level designations are $0-4s^2$, $1-4s4p$, $2-4p^2$, $3-4s6s$, $4-4s5p$. Laser pump radiation is indicated by straight lines, with fluorescence indicated by wavy lines.

Let the Ca $4s^2$ ground state be designated by 0 and the $4s4p$, $4p^2$, $4s6s$, and $4s\,5p$ excited states be designated 1, 2, 3, and 4, respectively (see Fig. 1). The pulsed dye laser creates an excited-state population $N_1(t)$ given by the rate equation

$$\frac{dN_1}{dt} = B_{01}N_0I_{01} - (A_{10} + B_{12}I_{12})N_1 + A_{21}N_2 \ . \tag{1}$$

Under the conditions prevailing in this experiment, depopulation of level 1 by the cw laser is insignificant compared to loss by spontaneous emission, with $B_{12}I_{12}$ typically a few percent of A_{01}. Similarly, repopulation by cascade is negligible so that $A_{21}N_2$ can be neglected as a source term. Therefore, Eq. (1) becomes

$$\frac{dN_1}{dt} = B_{01}N_0I_{01} - A_{10}N_1 \ . \tag{2}$$

The temporal evolution of $N_1(t)$ is determined by the time dependence of I_{01}, and the associated transition probabilities. It is therefore clear that if $I_{01}(t)$ is the same from shot-to-shot (on the average), then the time evolution of $N_1(t)$ will be independent of which transition the cw probe laser is pumping $(1\rightarrow 2)$ or $(1\rightarrow 3)$.

Detection of fluorescence radiation is by a photomultiplier whose anode current is integrated on a small capacitor producing a voltage $V=Q/C$, proportional to the time-integrated fluorescence. Let the total number of transitions to level 2 in one laser pulse be N_2^T. This will be given by

$$N_2^T = I_{12}B_{12}\int N_1(t)dt \; , \tag{3}$$

where I_{12} is the cw laser intensity, B_{12} is the Einstein B coefficient for the $(1\rightarrow 2)$ transition, and the integration is over the duration of the laser pulse. Clearly the detector voltage will be proportional to N_2^T.

Not all atoms in level 2 decay to level 1; a small fraction decay to level 4. The branching ratio will, therefore, multiply N_2^T. An exactly analogous expression can be found for N_3^T, which allows us to form the fluorescence ratio

$$R_F = \frac{N_3^T A_{31}(A_{21}+A_{24})}{N_2^T A_{21}(A_{31}+A_{34})} \; . \tag{4}$$

Using Eq. (3) and the fact that $N_1(t)$ is the same for either secondary excitation, the fluorescence ratio becomes

$$R_F = \frac{I_{13}B_{13}A_{31}(A_{21}+A_{24})}{I_{12}B_{12}A_{21}(A_{31}+A_{34})} \; . \tag{5}$$

The Einstein A and B coefficients are related by

$$B_{ik} = \frac{4\pi^3 c^2}{\hbar\omega_{ki}^3}\frac{g_k}{g_i}A_{ki} \; , \tag{6}$$

where g_k and g_i are the degeneracies of the upper and lower states, respectively. Since $\omega_{31}=\omega_{21}$ within experimental accuracy, one can relate the fluorescence ratio to transition probabilities by

$$R_F = \frac{g_3 I_{13} A_{31}^2 (A_{21}+A_{24})}{g_2 I_{12} A_{21}^2 (A_{31}+A_{34})} \; . \tag{7}$$

Occasionally, reliable lifetimes have been determined although the partial decay rates remain unknown. It is therefore of interest to point out that $(A_{21}+A_{24})^{-1}=\tau_2$, the lifetime of state 2, and likewise $\tau_3=(A_{31}+A_{34})^{-1}$. Solving for the unknown transition probability A_{31} in Eq. (7), and letting $I_{13}=I_{12}$, one obtains

$$A_{31} = A_{21}\left[\frac{R_F g_2 (A_{31}+A_{34})}{g_3(A_{21}+A_{24})}\right]^{1/2} \tag{8}$$

or, in terms of lifetimes,

$$A_{31} = A_{21}\left[\frac{R_F g_2 \tau_2}{g_3\tau_3}\right]^{1/2} \; . \tag{9}$$

Thus when reliable lifetimes are available these may be combined with the known A value and the measured fluorescence ratio to give the desired transition probability. Alternatively, if there is reason to believe that branching to other states is small so that, for example $A_{34}/A_{31} << 1$, then the fluorescence ratio can be used to determine directly the transition probability by

$$A_{31} = \frac{g_2}{g_3} R_F A_{21} \; . \tag{10}$$

III. APPARATUS

A schematic of the experimental apparatus is shown in Fig. 2. The calcium cell consisted of a stainless-steel cross of $1\frac{1}{2}$ in. diameter tubing 40 cm × 30 cm. Flanges were soldered to the ends of the cross and windows, mounted in place on *O*-ring seals. The ends of the cross were water cooled to protect the windows from calcium vapor. The calcium shot (99.9% pure) was loaded into a

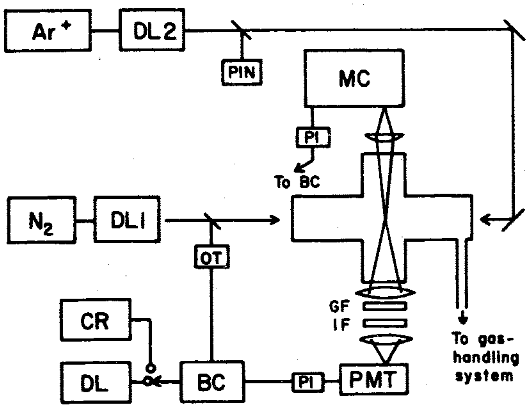

FIG. 2. Schematic of the experimental apparatus. Pulsed-laser radiation at 422.7 nm generated by dye laser (DL1) is directed in the stainless-steel vapor cell. The cw radiation at either 586.8 or 585.7 nm generated by DL2 is directed counter to DL1. Fluorescence is detected by either a monochromator (MC) or by the photomultiplier (PMT) after spectral selection by a glass filter (GF) and interference filter (IF). The preintegrated (PI) signals are routed to a boxcar integrator (BC) optically triggered (OT). The resultant signal may be recorded on either a strip-chart recorder (CR) or a data-logging system (DL).

stainless-steel boat with apertures for entrance and exit of the laser beams and with a slit on each side to allow detection of the fluorescence radiation. The oven was designed to allow heating of a section 12 cm × 20 cm of the cell to temperatures of 1000 °C, although temperatures in this experiment were much lower. Temperatures were measured by a Chromel-Alumel thermocouple strapped to the cross itself. The vapor cell was connected to a gas-handling system which allowed evacuation and back filling with a rare-gas buffer, in this case He. Pressures were measured by a Hg manometer.

The Ca $4s\,4p\ ^1P$ excited-state population was generated by a N_2-pulsed dye laser. The N_2 laser was designed after those described by Hilborn[4] and by Woodward *et al.*[5] The dye laser was a grazing-incidence design with output taken through a BK-7 glass wedge to reduce superfluorescence.[6,7] The bandwidth was estimated to be 0.02 nm from monochromator scans. Tuning was done with a differential micrometer allowing a precision of better than 0.01 nm. Stilbene 3 in methanol was used as the dye for 422.7-nm excitation of Ca. A small fraction of the pulsed dye laser (DL1) output was picked off and sent to a fast optical trigger[8] which in turn was used to trigger the detection electronics. The output of DL1 was weakly focused into the vapor cell. Attenuation of the DL1 beam was made by neutral density filters. Excitation from the Ca $4s\,4p$ state to ^1S and ^1D states was made by an Ar^+-pumped cw dye laser. The pump laser was a four-watt, Lexel, Ar^+ laser operating on the 514.5 nm line. The dye laser was a Spectra Physics 375 with a fine tuning etalon. The bandwidth was approximately 0.05 nm and the power was monitored by a calibrated *p-i-n* photodiode. The collimated cw laser beam was directed oppositely through the vapor cell relative to the pulsed dye-laser beam.

The emission at 422.7 nm was spectrally resolved and detected by a 0.35 m monochromator and multialkali photomultiplier. An image of the fluorescence region was rotated and focused by a periscope and quartz lens arrangement onto the entrance slit of the monochromator. Spectral scans of the 422.7-nm emission could be recorded on a strip-chart recorder. The emission at 585.7 nm and 586.8 nm was monitored by a dry-ice, cooled multialkali photomultiplier. Spectral selection was done by a 590.0 nm, three-cavity, interference filter tilted at 10° to bring its 10.0 nm band-pass down to 587 nm. Thus emission from both states could be monitored with the same filter arrangement which was spectrally flat over the 1.1 nm range of interest. In addition a Schott-glass GG-475 filter was used to block the intense 422.7 nm fluorescence. The outputs of both photomultipliers were first preintegrated[9] and the resultant shaped 200-μsec pulse routed to a boxcar integrator with a 100-μsec gate time centered on the pulse peak. The fluorescence intensity at 586 nm for each laser pulse was recorded by a data-logging system.

IV. MEASUREMENTS AND RESULTS

Data was taken at a calcium density of 6×10^{14} atoms/cm^3 as determined from the thermocouple temperature and the vapor pressure data specified by Nesmeyanov.[10] At densities much above this, attenuation of the 422.7-nm pump laser became excessive. For example, fluorescence at 422.7 nm for a calcium density of 1.8×10^{15} atom/cm^3 showed evidence of "hole-burning" as the laser power was increased. Even at the lower density, R_F is sensitive to saturation of the upper states at high DL2 probe powers. Data were taken at powers of 20 milliwatts and below to avoid the evident saturation which appears above 40 milliwatts. Data were taken for He buffer-gas pressures of 30 and 100 torr with no significant difference in the fluorescence ratio.

DL2 was tuned for peak fluorescence at each transition and data taken with both DL2 on and off. With DL1 alone a systematic background signal appeared possibly due to multiphoton or energy-pooling effects.[11] This component was subtracted from the two-photon signal and at worst amounted to 20% of the weaker 586.8-nm fluorescence. Data for each run were averaged and fluorescence ratios determined. Runs were made under varying conditions of buffer-gas pressure and laser power. Averaging the fluorescence ratios for those runs yields $R_F = (7.0\pm0.7)\times10^{-2}$, where the indicated uncertainty is the standard deviation of the mean. The two main sources of uncertainty in a given run appeared to be noise associated with the dc background due to blackbody radiation, and uncertainty due to tuning errors in consistently locating the fluorescence peak for 586.8 and 585.7 nm emission. Combining these uncertainties, I give $R_F = (7.0\pm1.0)\times10^{-2}$ as the best value for the fluorescence ratio.

If we can neglect branching, then Eq. (10) may be used to determine the A value. That this is a good approximation in our case can be seen by the close agreement of measured values for A_{21} and τ_2

TABLE I. Experimental and theoretical emission transition probabilities, oscillator strengths, and lifetimes.

Transition	λ (nm)	A_{expt} (10^7 sec^{-1})	A_{theor}	f_{theor}	τ^{-1} (10^7 sec^{-1})
$4s4p-4p^2$	585.7	6.6[b] 6.7[c]	7.6[d]	1.4−1.7[e]	6.7[f]
$4s4p-4s6s$	586.8	2.35[a]	1.8[d]		1.1[f]

[a] This work.
[b] Reference 13.
[c] Reference 16.
[d] Reference 1.
[e] Reference 2.
[f] Reference 14.

(see Table I).[12–14] A Bates and Damgaard[15] calculation for the branching ratio from the $4s6s\ ^1S$ state gives $A_{34}/A_{31}=0.03$. These low-branching ratios largely reflect the λ^{-3} dependence of A values. Using Eq. (7) will thus give rise to at most a few-percent error. From my measured fluorescence ratio and Smith and Raggett's[16] value for A_{21}, the transition probability for Ca ($4s6s\ ^1S \rightarrow 4s4p\ ^1P$) is, therefore, $A_{31}=2.35\times10^7$ sec^{-1}, with an uncertainty of 15%. The only theoretical value for the transition probability here determined is that of Hafner and Schwarz.[1] Their value is $A_{31}=1.8\times10^7$ sec^{-1}.

Note added in proof. Very recently Smith and Raggett[16] published a new value for the oscillator strength of the $4s4p\ ^1P_1$-$4p^2\ ^1D_2$ transition at 585.7 nm. Using their improved value as the reference lowers my A value for the 586.8 nm transition to 2.35×10^7 sec^{-1} and reduces the uncertainty to 15%.

I also point out that the oscillator strength listed by Smith and Raggett for the $4s4p\ ^1P_1$-$4s6s\ ^1S_0$ transition is at 551.2 nm indicating use of an early assignment for this wavelength. Bashkin and Stoner,[17] following Risberg,[18] designate the transition at 551.2 nm as $4s4p\ ^1P_1$-$4p^2\ ^1S_0$. I have followed the designation of Bashkin and Stoner.

V. ACKNOWLEDGMENTS

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